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(54) **SEQUENTIAL ELECTRODEPOSITION OF METALS USING MODULATED ELECTRIC FIELDS FOR MANUFACTURE OF CIRCUIT BOARDS HAVING FEATURES OF DIFFERENT SIZES**

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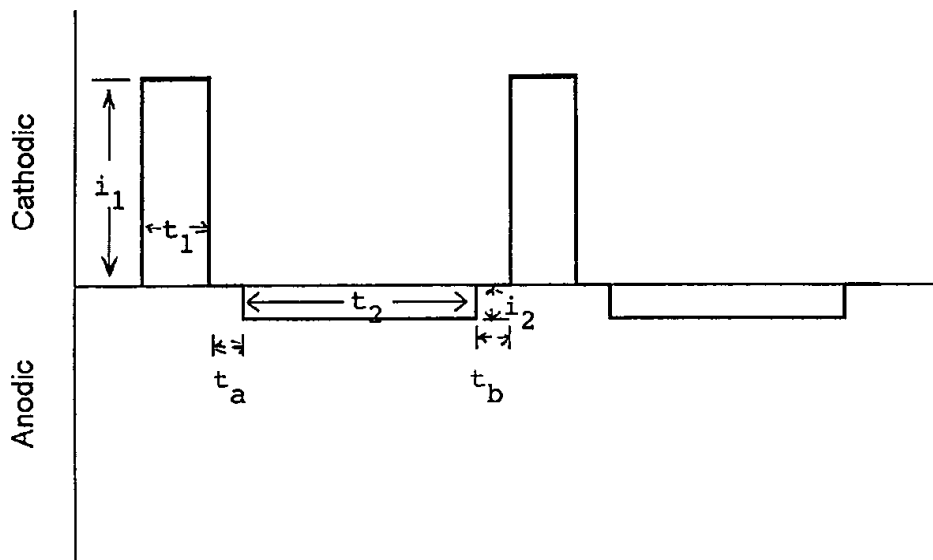
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ABSTRACT

A continuous layer of a metal is electrodeposited onto a substrate having both hydrodynamically inaccessible recesses and hydrodynamically accessible recesses on its surface by a twostep process in which the hydrodynamically inaccessible recesses are plated using a pulsed reversing current with cathodic pulses having a duty cycle of less than about 50% and anodic pulses having a duty cycle of greater than about 50% and the hydrodynamically accessible recesses are then plated using a pulsed reversing current with cathodic pulses having a duty cycle of greater than about 50% and anodic pulses having a duty cycle of less than about 50%.

(21) **Appl. No.:** 09/823,750(22) **Filed:** Apr. 3, 2001**Related U.S. Application Data**

(63) Continuation-in-part of application No. 09/419,881, filed on Oct. 18, 1999.



FIGS. 5 and 6 are photomicrographs showing cross sections of the substrate at each end of the through hole showing a generally uniform plating of the surface of the substrate and the interior surface of the through-hole, with minimum excessive plating ("dogboning") at the edge of the hole.

[0093] The invention having now been fully described, it should be understood that it may be embodied in other specific forms or variations without departing from its spirit or essential characteristics. Accordingly, the embodiments described above are to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

1. A method for depositing a continuous layer of a metal onto a substrate having small recesses in its surface comprising

immersing an electrically conductive substrate having a generally smooth surface having small recesses therein in an electroplating bath containing ions of a metal to be deposited onto said surface, said electroplating bath being substantially devoid of at least one member selected from the group consisting of levelers and brighteners,

immersing a counter electrode in said plating bath
passing an electric current between said electrodes,
wherein

said electric current is a modulated reversing electric current comprising pulses that are cathodic with respect to said substrate and pulses that are anodic with respect to said substrate,

the charge transfer ratio of said cathodic pulses to said anodic pulses is greater than one, and

the on-time of said first cathodic pulses ranges from about 0.83 microseconds to about 50 milliseconds and the on-time of said first anodic pulses is greater than the on-time of said cathodic pulses and ranges from about 42 microseconds to about 99 milliseconds.

in a second electroplating step, passing a second modulated reversing electric current between said electrodes, wherein said second modulated reversing electric current comprises second cathodic pulses and second anodic pulses,

said second cathodic pulses have a duty cycle greater than about 50% and said second anodic pulses have a duty cycle less than about 50%,

the charge transfer ratio of said second cathodic pulses to said second anodic pulses is greater than one, and

the frequency of said second pulses ranges from about 10 Hertz to about 5000 Hertz.

2. The method of claim 1 wherein an interval of no electric current flow is interposed between said cathodic pulses and succeeding anodic pulses.

3. The method of claim 1 wherein an interval of no electric current flow is interposed between said anodic pulses and succeeding cathodic pulses.

4. The method of claim 1 wherein an interval of no electric current flow is interposed between said cathodic pulses and succeeding anodic pulses and between said anodic pulses and succeeding cathodic pulses.

5. The method of claim 1 wherein, in said first electroplating step, said cathodic pulses and said anodic pulses succeed each other without intervening intervals of no electric current flow.

6. The method of claim 1 wherein, in said first electroplating step, said cathodic pulses and said anodic pulses form a pulse train having a frequency between about 50 Hertz and about 10000 Hertz.

7. The method of claim 1 wherein, in said first electroplating step, said cathodic pulses and said anodic pulses form a pulse train having a frequency between about 100 Hertz and about 6000 Hertz.

8. The method of claim 1 wherein, in said first electroplating step, said cathodic pulses and said anodic pulses form a pulse train having a frequency between about 500 Hertz and about 4000 Hertz.

9. The method of claim 1 wherein, in said first electroplating step, said cathodic pulses have a duty cycle of from about 30% to about 1%.

10. The method of claim 1 wherein, in said first electroplating step, said cathodic pulses have a duty cycle of from about 30% to about 15%.

11. The method of claim 1 wherein, in said first electroplating step, said cathodic pulses have a duty cycle of from about 30% to about 20%.

12. The method of claim 1 wherein, in said first electroplating step, said anodic pulses have a duty cycle of from about 60% to about 99%.

13. The method of claim 1 wherein, in said first electroplating step, said anodic pulses have a duty cycle of from about 70% to about 85%.

14. The method of claim 1 wherein, in said first electroplating step, said cathodic pulses have a duty cycle of from about 70% to about 80

15. The method of claim 1 wherein said metal is selected from the group consisting of copper, silver, gold, zinc, chromium, nickel, tin, lead, bronze, brass, solder, and alloys thereof.

16. The method of claim 1 wherein, in said first electroplating step, a layer of metal of substantially uniform thickness is deposited on said surface and within said hydrodynamically isolated recess.

17. The method of claim 1 wherein, in said first electroplating step, the thickness of the metal layer deposited within said hydrodynamically isolated recess is greater than the thickness of the metal layer deposited on said surface.

18. The method of claim 1 wherein, in said first electroplating step, said hydrodynamically isolated recess is substantially filled with metal.

19. The method of claim 1 wherein said hydrodynamically inaccessible recess has at least one transverse dimension not greater than about 350 micrometers.

20. The method of claim 1 wherein at least one transverse dimension of said hydrodynamically inaccessible recess is from about 5 micrometers to about 350 micrometers.

21. The method of claim 1 wherein at least one transverse dimension of said hydrodynamically inaccessible recess is from about 10 micrometers to about 250 micrometers.

22. The method of claim 1 wherein at least one transverse dimension of said hydrodynamically inaccessible recess is from about 25 micrometers to about 250 micrometers.

23. The method of claim 1 wherein at least one transverse dimension of said hydrodynamically inaccessible recess is from about 50 micrometers to about 150 micrometers.

24. A substrate having a surface with at least one hydrodynamically inaccessible recess in said surface, said substrate also having at least one hydrodynamically accessible recess, and said substrate having a layer of metal deposited in said hydrodynamically inaccessible recess by the first electroplating step of the process of claim 1.

25. The substrate of claim 24 wherein said metal layer is of substantially uniform thickness on said surface and on interior surfaces of said recess.

26. The substrate of claim 24 wherein said recesses are filled with metal.

27. The method of claim 1 wherein, in said second electroplating step, said cathodic pulses and said anodic pulses form a pulse train having a frequency between about 10 Hertz and about 4000 Hertz.

28. The method of claim 1 wherein, in said second electroplating step, said cathodic pulses and said anodic pulses form a pulse train having a frequency between about 10 Hertz and about 3000 Hertz.

29. The method of claim 1 wherein, in said second electroplating step, said cathodic pulses and said anodic pulses form a pulse train having a frequency between about 10 Hertz and about 1500 Hertz.

30. The method of claim 1 wherein, in said second electroplating step, said cathodic pulses have a duty cycle of from about 60% to about 99 %.

31. The method of claim 1 wherein, in said second electroplating step, said cathodic pulses have a duty cycle of from about 70% to about 95%.

32. The method of claim 1 wherein, in said second electroplating step, said cathodic pulses have a duty cycle of from about 85% to about 95%.

33. The method of claim 1 wherein, in said second electroplating step, said anodic pulses have a duty cycle of from about 40% to about 1%.

34. The method of claim 1 wherein, in said second electroplating step, said anodic pulses have a duty cycle of from about 30% to about 5%.

35. The method of claim 1 wherein, in said second electroplating step, said cathodic pulses have a duty cycle of from about 85% to about 5 %.

36. A circuit board having at least one major surface having thereon at least one electroplated high density interconnect area and at least one area having peripheral interconnect features, said circuit board having a layer of metal deposited thereon by the method of claim 1.

37. The method of claim 1 wherein in said first step said first cathodic pulses have a duty cycle less than about 50% and said first anodic pulses have a duty cycle greater than about 50%.

38. The method of claim 1 wherein in said first step said first cathodic pulses have an on-time and current density selected to produce electrodeposition under predominantly tertiary control and said anodic pulses have an on-time and current density selected to produce electroremoval of metal under predominantly primary and secondary control.

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Taylor et al. (43) **Pub. Date: Jan. 16, 2003**(54) **SEQUENTIAL ELECTRODEPOSITION OF METALS USING MODULATED ELECTRIC FIELDS FOR MANUFACTURE OF CIRCUIT BOARDS HAVING FEATURES OF DIFFERENT SIZES**(76) **Inventors:** E. Jennings Taylor, Troy, OH (US);
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Washington, DC 20036-5104 (US)(21) **Appl. No.:** 10/132,399(22) **Filed:** Apr. 26, 2002**Related U.S. Application Data**

(63) Continuation-in-part of application No. 09/823,750, filed on Apr. 3, 2001, which is a continuation-in-part of application No. 09/419,881, filed on Oct. 18, 1999, now Pat. No. 6,309,528.

(60) Provisional application No. 60/159,541, filed on Oct. 15, 1999.

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H05K 3/00(52) **U.S. Cl.** 205/103; 205/118; 205/122;
205/125; 205/131; 205/136(57) **ABSTRACT**

A continuous layer of a metal is electrodeposited onto a substrate having both hydrodynamically inaccessible recesses and hydrodynamically accessible recesses on its surface by a two-step process in which the hydrodynamically inaccessible recesses are plated using a pulsed reversing current with cathodic pulses having a duty cycle of less than about 50% and anodic pulses having a duty cycle of greater than about 50% and the hydrodynamically accessible recesses are then plated using a pulsed reversing current with cathodic pulses having a duty cycle of greater than about 50% and anodic pulses having a duty cycle of less than about 50%.

about 30% and more preferably from about 5% to about 15%. FIG. 3C shows a schematic cross section of the circuit board 300 after the second step of the process. A uniform layer 326 of copper has been deposited over the first layer 324 and onto the inner surface 322 of the through-hole 320. The uniformly plated board 300 can then be masked, imaged and etched by conventional procedures to provide conductive traces on the surfaces 302 of the board 300.

EXAMPLE

[0097] This example illustrates the preparation of a substrate having filled vias and a uniform surface deposit of copper by the process of the invention.

[0098] In order to provide a substrate having vias and through holes similar to those found in a multi-layer circuit board, small blind holes having a diameter of about 75-100 micrometers were drilled in the surface of a brass panel having dimensions of 18 inches \times 8 inches using a laser. Through holes having a diameter of about 325 micrometers were also made in the plate using a mechanical drill. The plate was mounted in a conventional industrial circuit board electroplating apparatus and plated in two steps according to the invention.

[0099] The plating bath had the following composition: 60-65 g/L of copper sulfate, 166 g/L of sulfuric acid, about 50 parts per million (ppm) of chloride ion, and about 300 ppm of polyethylene glycol (PEG).

[0100] In the first step of the plating process the pulsed reversing electric current had the following characteristics: cathodic duty cycle, 33%; anodic duty cycle, 67%; average cathodic current density, 25 amperes per square foot (ASF), frequency of pulse train, about 333 Hz, and cathodic/anodic charge ratio (Q_c/Q_a), 2.5. The plating was conducted for a period of 3 hours in the first step.

[0101] The second step of the plating process was then conducted by merely changing the waveform of the plating current. The bath was not changed, the board was not removed from the plating apparatus and no other processing steps were conducted.

[0102] In the second step of the plating process the pulsed, reversing electric current had the following characteristics: cathodic duty cycle, 90%; anodic duty cycle, 10%; average cathodic current density, 25 amperes per square foot (ASF), frequency of pulse train, about 100 Hz, and cathodic/anodic charge ratio (Q_c/Q_a), 10. The plating was conducted for a period of 1 hour in the second step.

[0103] The results achieved are illustrated in FIGS. 4-6. FIG. 4 is a photomicrograph of a cross-section of the plated substrate showing the vias filled with deposited copper. (Certain defects in the brass test panel are also visible.) FIGS. 5 and 6 are photomicrographs showing cross sections of the substrate at each end of the through hole showing a generally uniform plating of the surface of the substrate and the interior surface of the through-hole, with minimum excessive plating ("dogboning") at the edge of the hole.

[0104] The invention having now been fully described, it should be understood that it may be embodied in other specific forms or variations without departing from its spirit or essential characteristics. Accordingly, the embodiments described above are to be considered in all respects as

illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

We claim:

1. A method for depositing a continuous layer of a metal onto a substrate having both hydrodynamically inaccessible recesses and hydrodynamically accessible recesses on its surface comprising,

immersing, as an electrode, an electrically conductive substrate having a generally smooth surface having at least one hydrodynamically inaccessible recess and at least one hydrodynamically accessible recess in said surface in an electroplating bath containing ions of a metal to be deposited onto said surface, said electroplating bath being substantially devoid of at least one additive selected from the group consisting of levelers and brighteners;

immersing a counterelectrode in said plating bath;

preferentially depositing metal into said hydrodynamically isolated recesses by passing a first modulated reversing electric current between said electrodes, wherein

said first modulated reversing electric current comprises a first pulse train of first cathodic pulses and first anodic pulses, with respect to said electrically conductive substrate,

the charge transfer ratio of said first cathodic pulses to said first anodic pulses is greater than one,

said first cathodic pulses have an on-time ranging from about 0.83 microseconds to about 200 milliseconds, and

said first anodic pulses have an on-time greater than the on-time of said first cathodic pulses and ranging from about 42 microseconds to about 198 milliseconds; and

preferentially depositing metal into said hydrodynamically accessible recesses by passing a second modulated reversing electric current between said electrodes, wherein

said second modulated reversing electric current comprises a second pulse train of second cathodic pulses and second anodic pulses,

the charge transfer ratio of said second cathodic pulses to said second anodic pulses is greater than one,

said second cathodic pulses have an on-time ranging from about 0.12 milliseconds to about 198 milliseconds,

said second anodic pulses have an on-time shorter the on-time of said second cathodic pulses and ranging from about 2 microseconds to about 60 milliseconds.

2. The method of claim 1, wherein an interval of no electric current flow is interposed between said cathodic pulses and succeeding anodic pulses.

3. The method of claim 1, wherein an interval of no electric current flow is interposed between said anodic pulses and succeeding cathodic pulses.

4. The method of claim 1, wherein an interval of no electric current flow is interposed between said cathodic pulses and succeeding anodic pulses and between said anodic pulses and succeeding cathodic pulses.

5. The method of claim 1, wherein, in said first pulse train, said cathodic pulses and said anodic pulses succeed each other without intervening intervals of no electric current flow.

6. The method of claim 1, wherein, in said first pulse train, said cathodic pulses have an on-time ranging from about 1 microsecond to about 10 milliseconds.

7. The method of claim 1, wherein, in said first pulse train, said cathodic pulses have an on-time ranging from about 1.7 microseconds to about 5 milliseconds.

8. The method of claim 1, wherein, in said first pulse train, said cathodic pulses have an on-time ranging from about 2.5 microseconds to about 1 millisecond.

9. The method of claim 1, wherein, in said first pulse train, said anodic pulses have an on-time ranging from about 50 microseconds to about 19.8 milliseconds.

10. The method of claim 1, wherein, in said first pulse train, said anodic pulses have an on-time ranging from about 84 microseconds to about 9.9 milliseconds.

11. The method of claim 1, wherein, in said first pulse train, said anodic pulses have an on-time ranging from about 125 microseconds to about 1.98 milliseconds.

12. The method of claim 1, wherein the frequency of said first pulse train is between about 5 Hertz and about 12000 Hertz.

13. The method of claim 1 wherein wherein the frequency of said first pulse train is between about 100 Hertz and about 10000 Hertz.

14. The method of claim 1 wherein wherein the frequency of said first pulse train is between about 200 Hertz and about 4000 Hertz.

15. The method of claim 1 wherein wherein the frequency of said first pulse train is between about 200 Hertz and about 2000 Hertz.

16. The method of claim 1 wherein, in said first pulse train, said cathodic pulses have a duty cycle of from about 30% to about 1%.

17. The method of claim 1 wherein, in said first pulse train, said cathodic pulses have a duty cycle of from about 30% to about 15%.

18. The method of claim 1 wherein, in said first pulse train, said cathodic pulses have a duty cycle of from about 30% to about 20%.

19. The method of claim 1 wherein, in said first pulse train, said anodic pulses have a duty cycle of from about 60% to about 99%.

20. The method of claim 1 wherein, in said first pulse train, said anodic pulses have a duty cycle of from about 70% to about 85%.

21. The method of claim 1 wherein, in said first pulse train, said cathodic pulses have a duty cycle of from about 70% to about 80%.

22. The method of claim 1, wherein, in said second pulse train, said cathodic pulses have an on-time ranging from about 0.14 milliseconds to about 170 milliseconds.

23. The method of claim 1, wherein, in said second pulse train, said cathodic pulses have an on-time ranging from about 0.14 milliseconds to about 160 milliseconds.

24. The method of claim 1, wherein, in said second pulse train, said anodic pulses have an on-time ranging from about 2 microseconds to about 60 milliseconds.

25. The method of claim 1, wherein, in said second pulse train, said anodic pulses have an on-time ranging from about 30 microseconds to about 60 milliseconds.

26. The method of claim 1, wherein, in said second pulse train, said anodic pulses have an on-time ranging from about 40 microseconds to about 60 milliseconds.

27. The method of claim 1, wherein said second pulse train has a frequency between about 5 Hertz and about 4000 Hertz.

28. The method of claim 1, wherein said second pulse train has a frequency between about 10 Hertz and about 2500 Hertz.

29. The method of claim 1, wherein said second pulse train has a frequency between about 20 Hertz and about 1000 Hertz.

30. The method of claim 1, wherein said second pulse train has a frequency between about 50 Hertz and about 200 Hertz.

31. The method of claim 1, wherein, in said second pulse train, said cathodic pulses have a duty cycle of from about 60% to about 99%.

32. The method of claim 1, wherein, in said second pulse train, said cathodic pulses have a duty cycle of from about 70% to about 95%.

33. The method of claim 1, wherein, in said second pulse train, said cathodic pulses have a duty cycle of from about 80% to about 95%.

34. The method of claim 1, wherein, in said second pulse train, said anodic pulses have a duty cycle of from about 40% to about 1%.

35. The method of claim 1, wherein, in said second pulse train, said anodic pulses have a duty cycle of from about 30% to about 5%.

36. The method of claim 1, wherein, in said second pulse train, said anodic pulses have a duty cycle of from about 20% to about 5%.

37. The method of claim 1, wherein said metal is selected from the group consisting of copper, silver, gold, zinc, chromium, nickel, tin, lead, bronze, brass, solder, and alloys thereof.

38. The method of claim 1, wherein said hydrodynamically inaccessible recess has at least one transverse dimension not greater than about 350 micrometers.

39. The method of claim 1, wherein at least one transverse dimension of said hydrodynamically inaccessible recess is from about 5 micrometers to about 350 micrometers.

40. The method of claim 1, wherein at least one transverse dimension of said hydrodynamically inaccessible recess is from about 10 micrometers to about 250 micrometers.

41. The method of claim 1, wherein at least one transverse dimension of said hydrodynamically inaccessible recess is from about 25 micrometers to about 250 micrometers.

42. The method of claim 1, wherein at least one transverse dimension of said hydrodynamically inaccessible recess is from about 50 micrometers to about 150 micrometers.

43. A substrate having a surface with at least one hydrodynamically inaccessible recess in said surface, said substrate also having at least one hydrodynamically accessible recess, and said substrate having a layer of metal deposited in said hydrodynamically inaccessible recess by the first electroplating pulse train of the process of claim 1.

44. The substrate of claim 24 wherein said metal layer is of substantially uniform thickness on said surface and on interior surfaces of said recess.

45. The substrate of claim 24 wherein said recesses are filled with metal.

46. A circuit board having at least one major surface having thereon at least one electroplated high density interconnect area and at least one area having peripheral interconnect features, said circuit board having a layer of metal deposited thereon by the method of claim 1.

47. The method of claim 1 wherein in said first pulse train said first cathodic pulses have a duty cycle less than about 50% and said first anodic pulses have a duty cycle greater than about 50%.

48. The method of claim 1 wherein in said first pulse train said first cathodic pulses have an on-time and current density selected to produce electrodeposition under predominantly tertiary control and said first anodic pulses have an on-time and current density selected to produce electroremoval of metal under predominantly primary and secondary control.

49. The method of claim 1 wherein said plating bath is substantially devoid of brighteners.

50. The method of claim 1 wherein said plating bath is substantially devoid of levelers.

51. The method of claim 1 wherein said plating bath is substantially devoid of brighteners and levelers.

52. The method of claim 1 wherein said metal is copper and said plating bath contains a suppressor.

53. The method of claim 52, wherein said suppressor is present in an amount of from about 100 parts per million to about 5% by weight of said plating bath.

54. The method of claim 52, wherein said suppressor is present in an amount of from about 200 parts per million to about 800 parts per million by weight of said plating bath.

55. The method of claim 52, wherein said suppressor is present in an amount of about 300 parts per million by weight of said plating bath.

56. The method of claim 52, wherein said suppressor is an organic polyhydroxy compound.

57. The method of claim 52, wherein said suppressor is poly(ethylene glycol).

58. The method of claim 52, wherein said poly(ethylene glycol) has a molecular weight in the range of from about 1000 to about 12000.

59. The method of claim 52, wherein said poly(ethylene glycol) has a molecular weight in the range of from about 2500 to about 5000.

60. The method of claim 52, wherein said bath contains chloride ion in a concentration of about 40 parts per million by weight to about 200 parts per million by weight.

61. The method of claim 52, wherein said bath contains chloride ion in a concentration of about 50 parts per million by weight.

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